

# Direct observation of $R...R$ distances in rare-earth ( $R$ ) phosphate glasses by magnetic difference neutron diffraction

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A magnetic difference neutron diffraction study of a rare-earth (Tb) phosphate glass has revealed exclusively the Tb...Tb distances. The difference between data taken with and without an applied magnetic field of 4 T shows Tb...Tb pairwise atomic correlations at 3.9 and 6.4 Å, respectively, with relative coordination numbers of 1:14. The first distance arises when two Tb<sup>3+</sup> ions share a common oxygen neighbor, and indicates a clustering of rare-earth ions. The second distance arises when two Tb<sup>3+</sup> ions are coordinated to different oxygens in the same PO<sub>4</sub> group, in a near-linear arrangement.

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Rare-earth ( $R$ ) phosphate glasses show promise in the laser and optoelectronics industry, on account of their favorable population inversion and magnetic characteristics. The structural nature of these glasses dictates their physical properties, especially the closest  $R...R$  approach, since too close a separation impairs their optical and magnetic phenomena.

Conventional x-ray<sup>1-5</sup> and neutron<sup>4,6</sup> diffraction, extended x-ray absorption fine structure (EXAFS),<sup>1,7</sup> x-ray absorption near-edge structure<sup>8</sup> and solid-state NMR<sup>3,6</sup> studies on glasses, (R<sub>2</sub>O<sub>3</sub>)<sub>x</sub>(P<sub>2</sub>O<sub>5</sub>)<sub>1-x</sub>, where 0.167 (ultraphosphate)  $< x < 0.25$  (metaphosphate) have, in combination, been able to piece together local structure out to an interatomic distance  $r$  of about 4 Å (see Fig. 5 in Ref. 3). However, the  $R...R$  separation is not part of this defined local structure, and beyond this 4 Å radial limit these standard characterization techniques are uninformative, owing to (i) increasing numbers of overlapping pairwise correlations in conventional diffraction; (ii) progressively damped signal, and obscuring multiple scattering effects in EXAFS; and (iii) the inherent short-range  $J$ - $J$  coupling effects, and heavily broadened signal, in NMR.

We report the use of a technique that provides direct experimental evidence for the minimum  $R...R$  separation in a rare-earth phosphate glass. The experiment exploits magnetic difference neutron diffraction methods using the General Materials time-of-flight diffractometer (GEM)<sup>9</sup> at the ISIS Facility, UK. Neutron diffraction measurements using both magnetic and temperature differences have previously been reported in the literature as a means of investigating the magnetic structure in *crystalline* compounds (for example, see Lynn *et al.*<sup>10</sup>). In our study, a magnetic difference diffraction measurement has been used as a means of investigating the atomic structure of an *amorphous* material.

The experimental methodology behind the experiment<sup>11</sup> relies on the exploitation of the intrinsic paramagnetism of the rare-earth ions, and is performed in two parts. Firstly, the neutron diffraction pattern of the glass at low temperature is measured by conventional means, except that data acquisition times are unusually long so as to obtain particularly high

counting statistics. Secondly, an external magnetic field is applied to the sample, and the measurement, which is otherwise identical, is repeated. The magnetic field increases the degree of alignment of the magnetic moments of the rare-earth ions in the sample, and this manifests itself as an enhancement of the contribution to the diffraction pattern arising from the interference between the scattering from the magnetic ions. Therefore, the difference in the resulting diffraction patterns,  $I(Q)_{\text{field-on}} - I(Q)_{\text{field-off}}$ , yields exclusively the magnetically induced perturbation of the  $R...R$  scattering contribution. The corresponding Fourier transform of this difference thence affords all  $R...R$  separations, via pairwise correlations.

A (Tb<sub>2</sub>O<sub>3</sub>)<sub>0.246</sub>(P<sub>2</sub>O<sub>5</sub>)<sub>0.722</sub>(Al<sub>2</sub>O<sub>3</sub>)<sub>0.032</sub> glass was prepared by heating 25 mol. % of high purity (99.9%) rare-earth oxide in the presence of excess P<sub>2</sub>O<sub>5</sub> in an aluminum oxide crucible at a temperature of 1650 °C. Full synthetic details are described elsewhere.<sup>12</sup> The sample composition was determined by electron probe microanalysis (EPMA).

The 6.54 g powdered sample, tightly packed into a cylindrical vanadium container, was cooled to 4 K using an Oxford Instruments cryomagnet, and held at this temperature throughout in order to ensure that the magnetic susceptibility was saturated, and therefore that the greatest practicable contrast between the two diffraction patterns is realized. Previous studies show that the data collection temperature makes negligible difference upon the amorphous structure in the absence of an external magnetic field.<sup>3</sup> Data were collected without an external magnetic field for 41.5 h, and then with a field of 4 T applied for 42.6 h under otherwise identical experimental conditions. The data were normalized with respect to scattering from a vanadium rod. Standard container, background, absorption, and multiple scattering corrections were applied<sup>13</sup> to yield a corrected diffraction pattern  $I(Q)$ , where  $\hbar Q$  is the momentum transfer for scattering. Magnetization measurements<sup>11,14</sup> show that at temperatures down to 2.4 K terbium metaphosphate glass is paramagnetic, and that a field of 4 T is sufficient to cause the magnetization to begin to approach saturation. Therefore, the “field off” data corre-

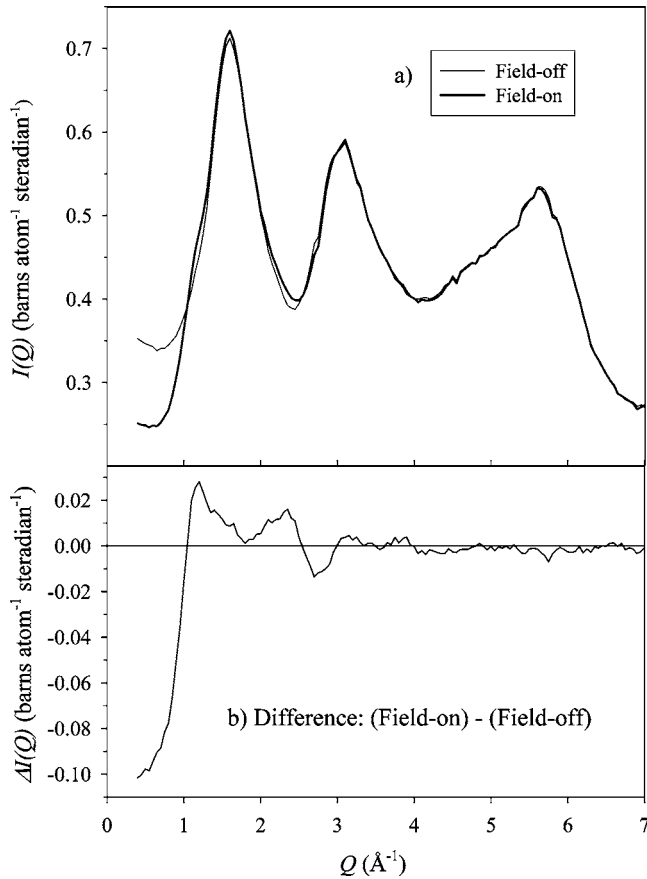


FIG. 1. The diffraction patterns for  $(\text{Tb}_2\text{O}_3)_{0.246}(\text{P}_2\text{O}_5)_{0.722}(\text{Al}_2\text{O}_3)_{0.032}$  glass at 4 K, showing (a) the full diffraction pattern  $I(Q)$ , with and without the application of the 4 T magnetic field, and (b) the field-on minus field-off difference  $\Delta I(Q)$ .

spond to a situation where there is small correlation between the moments of  $\text{Tb}^{3+}$  ions, while the “field on” data correspond to a situation where there is significant correlation between the magnetic moments. This explains the origin of the effect that we have observed.

The difference between the two diffraction patterns  $[\Delta I(Q)]$ , field on – field off, is shown in Fig. 1. The oscillatory difference becomes negligible at a maximum momentum transfer,  $Q_{\text{max}} \sim 7 \text{ \AA}^{-1}$ , which corresponds well to the extent of the  $\text{Tb}^{3+}$  magnetic form factor.<sup>15</sup> The data were Fourier transformed according to

$$D(r) = \frac{2}{\pi} \int_0^{Q_{\text{max}}} Q [I(Q) - I^{\text{self}}(Q)] M(Q) \sin(rQ) dQ, \quad (1)$$

to provide the differential correlations  $D(r)$  and  $\Delta D(r)$ , shown in Fig. 2.  $M(Q)$  is the Lorch modification function and  $I^{\text{self}}(Q)$  is the calculated sum of the nuclear and magnetic self scattering. The peaks of  $\Delta D(r)$  represent frequently occurring Tb...Tb separations, except for the peak below 1 Å that arises from experimental errors. The first two Tb...Tb peaks in  $\Delta D(r)$  were simulated, taking into account the effect on the real-space peak function of the magnetic form factor of the  $\text{Tb}^{3+}$  ions, so as to reveal the average Tb...Tb sepa-

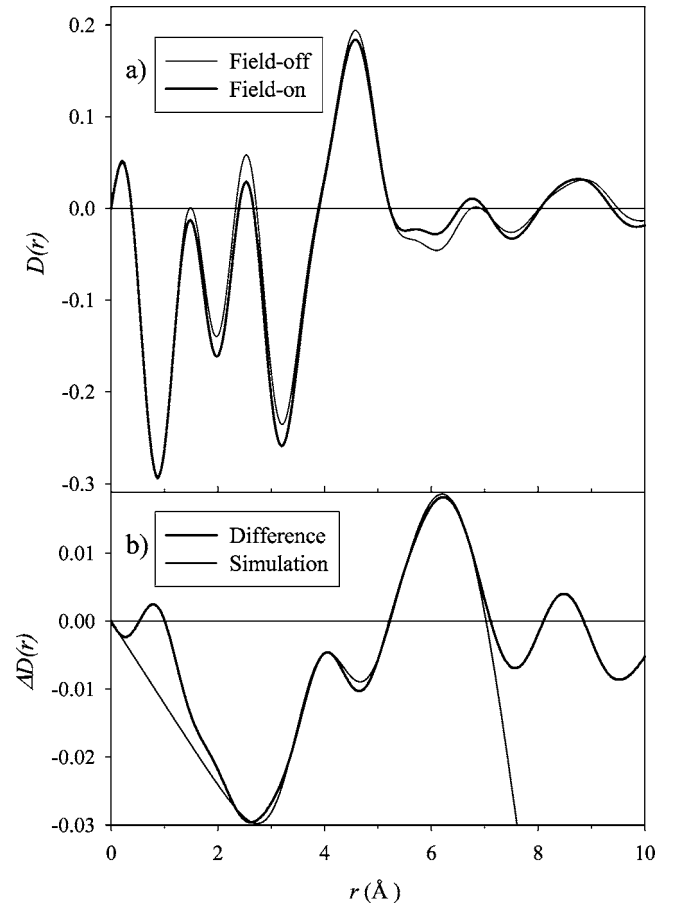


FIG. 2. The correlation functions for  $(\text{Tb}_2\text{O}_3)_{0.246}(\text{P}_2\text{O}_5)_{0.722}(\text{Al}_2\text{O}_3)_{0.032}$  glass at 4 K, showing (a) the correlation function  $D(r)$  (arbitrary units), with and without the application of the 4 T magnetic field, and (b) the field-on minus field-off difference  $\Delta D(r)$ . Also shown is the simulation of the first two distances in  $\Delta D(r)$  described in the text.

ration,  $r_{\text{TbTb}}$ , the rms variation in interatomic distance,  $\langle u^2 \rangle^{1/2}$ , and their relative coordination number derived from the peak areas in  $\Delta D(r)$  (see Table I). A linear term  $-0.0122r$  was included to take into account the average magnetization contribution. Further details are described in Ref. 16.

Given that the  $\text{Tb}_2\text{O}_3$  content of our glass sample lies between the ultra- and metaphosphate compositions, where analogous crystal structures have been determined, it would seem pertinent to consider the results relative to  $R \dots R$  separations in these regular structures. The shortest  $R \dots R$  separation in rare-earth meta- and ultraphosphate crystal structures<sup>17</sup> ranges over 4.234–5.537 Å and 5.148–6.288 Å,

TABLE I. Parameters for the simulation of the first two peaks in  $\Delta D(r)$ .

Peak	$r_{\text{TbTb}}$ (Å)	$\langle u^2 \rangle^{1/2}$ (Å)	Area (arb. units)	Relative coordination number
1	3.9	0.2	0.036	1.0
2	6.4	1.2	0.31	14.1

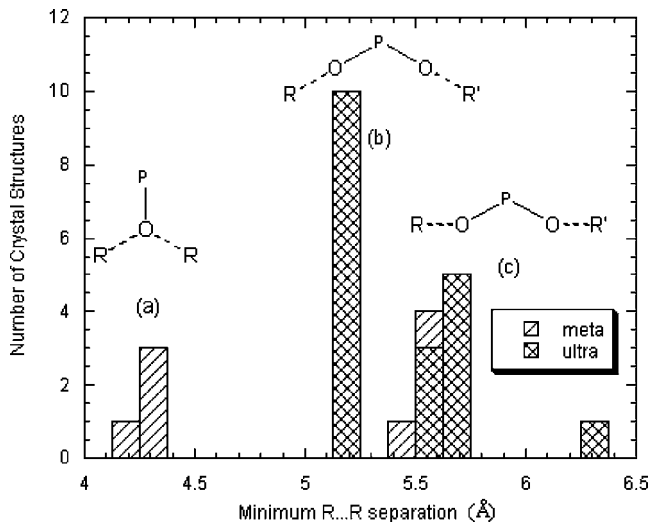


FIG. 3. A histogram of the shortest  $R...R$  separations in all known rare-earth metaphosphate ( $RP_3O_9$ ) and ultraphosphate ( $RP_5O_{14}$ ) crystal structures. The three main types of  $R...R$  separation expected in these glasses up to  $\sim 7$  Å are: (a)  $R(O)-R'$  configuration as found in orthorhombic metaphosphate crystals, (b) V-shaped  $R(OPO)-R'$  configuration as found in ultraphosphate and monoclinic metaphosphate crystals, and (c) approximately linear  $R(OPO)-R'$  configuration as found in orthorhombic metaphosphate crystals.

respectively, in a distinctly bimodal distribution (see Fig. 3). Significantly, the mode corresponding to 4.2–4.3 Å is characteristic of all C-centered orthorhombic polymorphs of rare-earth metaphosphates<sup>18</sup> and corresponds to the correlation  $R(O)-R'$ , where  $R$  and  $R'$  represent two different  $R^{3+}$  ions that coordinate to a common O in a  $PO_4$  phosphate group [see Fig. 3(a)]. The same configuration is also found in crystals with more than 25 mol. %  $R_2O_3$ . The peak centered at 3.9 Å in this study is therefore indicative of the presence of this metaphosphate-like structural motif in the glass. The results are also consistent with a previous reverse Monte Carlo (RMC) simulation<sup>19</sup> whose starting parameters were based on crystal structure  $R...R$  separations and therefore relate to the present arguments.

The second modal distribution shown in Fig. 3 corresponds to the minimum  $R...R$  separation in ultraphosphate crystals.<sup>20</sup> This distance arises from an  $R(OPO)-R'$  correlation where the rare earths  $R$  and  $R'$  are coordinated to two different oxygens in a phosphate group in a V-shaped formation [Fig. 3(b)]. The presence of this ultraphosphate-like structural motif in the glass would lead to a feature in  $\Delta D(r)$  in the range 5.2–5.7 Å, and in fact the major peak centered at 6.4 Å shows some asymmetry with a shoulder at about this distance. It is important to note that the few crystalline metaphosphate structures that fall into this predominantly ultraphosphate modal distribution exist in different space groups (both monoclinic:  $Pm$  and  $P2_1/c$ ) to all other metaphosphates; their minimum  $R...R$  separations relate to a similar V-shaped  $R(OPO)-R'$  correlation. The notable gap between the two modes in Fig. 3 rationalizes our ability to resolve easily the peaks that are associated with  $R(O)-R'$  and V-shaped  $R(OPO)-R'$  structural motifs in our  $\Delta D(r)$  profile.

The second  $R...R$  separation observed in  $\Delta D(r)$  is centered at the same distance, 6.4 Å, as Hoppe *et al.*<sup>5</sup> have deduced by means of a RMC simulation. In the current study, a direct observation of this  $R...R$  correlation is reported. Hoppe *et al.*<sup>5</sup> found that the  $R...R$  distance of 6.4 Å arose from

$R(OPO)-R'$  configurations in the RMC-simulated glass structure. Trigonometric calculations based on the average  $R-O$  and  $O(P)-O'$  separations taken from previous x-ray diffraction data<sup>3</sup> show that this distance corresponds more closely to a linear, rather than V-shaped,  $R(OPO)-R'$  configuration [5.5 Å (V-shaped) - 7 Å (linear)] on average given the wide variation revealed. In orthorhombic metaphosphate crystalline analogs<sup>18</sup> the second-nearest  $R...R$  distance lies at about 7 Å and arises from an almost linear  $R(OPO)-R'$  configuration [Fig. 3(c)]. We would expect the distribution center (6.4 Å) to be foreshortened from this linear distance due to the aforementioned shoulder arising from a minor ultraphosphate-like minimum  $R...R$  separation in the range 5.2–5.7 Å. We deduce, therefore, that linear  $R(OPO)-R'$  configurations, indicative of the C-centered orthorhombic metaphosphate type motif, are largely responsible for the correlation centered at 6.4 Å. In the range, 5.5–7 Å, there are also several contributions possible from second- and third-neighbor  $R...R$  correlations reminiscent of those observed in monoclinic metaphosphate, monoclinic ultraphosphate, or orthorhombic ultraphosphate analogs, but they would appear much more diffuse given their low frequency (1–2 per rare-earth ion) compared with the dominance of orthorhombic metaphosphate type structural motifs (8 around 7 Å per rare-earth ion).

Furthermore, the RMC simulation of Hoppe *et al.*<sup>5</sup> showed that a prepeak feature in the x-ray first sharp diffraction peak (FSDP) that is associated with the second  $R...R$  separation, is observable only if the composition of  $(R_2O_3)_x(P_2O_5)_{1-x}$  is such that  $x > 0.16$ , i.e., exceeding the ultraphosphate composition. Such a trend is also observable in our previous x-ray diffraction data.<sup>3</sup>

There are important physical implications of these findings. The 3.9 Å minimum  $R...R$  separation revealed here shows that rare-earth ion clustering must be present; a random homogeneous distribution of  $Tb^{3+}$  ions (as calculated purely from density and stoichiometric values) would yield an *average*  $Tb...Tb$  separation of 6.05 Å, which is considerably in excess of the measured distance of 3.9 Å. Secondly, the 3.9 and 6.4 Å peaks both seem to reflect a metaphosphate-like structural motif, and therefore will occur together. Combining this with the fact that the FSDP associated with the 6.4 Å peak is evident in all of our series of rare-earth phosphate glasses<sup>3</sup> indicates that rare-earth clustering is present in all such glasses where  $0.167 < x < 0.25$ . These results are consistent with the model of Hoppe *et al.*<sup>5</sup>

For the less  $R_2O_3$ -rich glass compositions, below the ultraphosphate composition, the model of Hoppe *et al.*<sup>5</sup> indicates the complete loss of both the  $R(O)-R'$  correlation, which we observe at 3.9 Å, and the FSDP, which is attributed to the near-linear  $R(OPO)-R'$  correlations at 6.4 Å. For such compositions the minimum  $R...R$  separation would then arise from V-shaped  $R(OPO)-R'$  correlations in the region of 5.4 Å.

Another way of achieving primarily V-shaped  $R$ -(OPO)- $R'$  configurations, at the expense of 3.9 and 6.4 Å metaphosphate-type motifs, is to incorporate  $\text{Al}^{3+}$  ions within the framework.  $\text{Al}^{3+}$  ions may enter the network in 6, 5, or 4 coordinated sites, as shown by solid-state NMR studies<sup>6</sup> on samples in which  $\text{Al}^{3+}$  impurities were present in only small quantities (typically 1–2 wt. %). Martin *et al.*<sup>21</sup> used isomorphous substitution neutron diffraction on  $(\text{R}_2\text{O}_3)_{0.230}(\text{P}_2\text{O}_5)_{0.701}(\text{Al}_2\text{O}_3)_{0.069}$  ( $R=\text{Dy}$  or  $\text{Ho}$ ) glass, which has a much higher  $\text{Al}_2\text{O}_3$  content, and found that their real-space function is dominated by a peak at 5.62 Å.  $R$ -(OPO)- $R'$  correlations at 6.4 Å are negligible. Martin *et al.*<sup>21</sup> did not report any peak in the vicinity of 3.9 Å, although we note that a peak at 4.72 Å was identified, but dismissed. These results, combined with those reported here, indicate that the  $\text{Al}_2\text{O}_3$  content of the glass may have a major impact on the  $R\dots R$  correlations. Nevertheless, it should be noted that the isomorphous substitution technique, as used by Martin *et al.*<sup>21</sup> to isolate  $R\dots X$  correlations ( $X=R$ ,  $\text{P}$ , or  $\text{O}$ ), is intrinsically less reliable than the magnetic difference technique used here, because it involves taking a difference between diffraction data from two distinct glass samples containing different rare earths, which must be assumed to be equivalent. The magnetic difference technique uses only one sample and hence is not subject to these reliability concerns.

To conclude, our salient findings are that  $\text{R}^{3+}$  ion clustering is present in rare-earth phosphate glasses,  $(\text{R}_2\text{O}_3)_x(\text{P}_2\text{O}_5)_{1-x}$ , that have compositions between the ultra- ( $x=0.167$ ) and metaphosphate ( $x=0.25$ ) limits. A minimum  $R\dots R$  separation of 3.9 Å is observed, and arises from metaphosphate-like  $R$ -(O)- $R'$  configurations. The first direct

evidence of a second, much stronger correlation at 6.4 Å is reported, and this distance corresponds well to a second-neighbor linear metaphosphate-like  $R$ -(OPO)- $R'$  configuration. Although both of these features more closely resemble metaphosphate crystals, a small shoulder present in the second real-space peak in the range 5.2–5.7 Å suggests that a minor proportion of correlations have a V-shaped  $R$ -(OPO)- $R'$  form. Comparison with other types of experiments in the literature<sup>21</sup> support our proposition that, in glasses where the  $R\dots R$  real-space correlation function is dominated by a peak at about 5.4 Å, the V-shaped  $R$ -(OPO)- $R'$  form dominates such that the correlations at 3.9 and 6.4 Å are negligible. There thus appear to be two different dominant types of  $R$ -(OPO)- $R'$  correlation, either near-linear or V-shaped, and each type forms at the expense of the other. From a materials-centered perspective it is generally preferable for the rare-earth ions to be well separated, and it appears that one may be able to tailor these glasses to suit a desired optical and magnetic property by judiciously changing the  $\text{R}_2\text{O}_3$  content  $x$ , or by adding a suitable level of  $\text{Al}^{3+}$  ions.

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